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Effect of Si substitution on structural, electronic and optical properties of YNi_4Si-type $DyNi_{5-x}Si_x$ ($x=0, 1, 2$) compounds

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ABSTRACT

We employed first principle calculations for investigation of structural, electronic and optical properties of YNi_4Si-type $DyNi_{5-x}Si_x$ ($x=0, 1, 2$) compounds. These properties are studied first time on YNi_4Si-type $DyNi_{5-x}Si_x$ compounds. The exchange and correlation potential is treated by the Coulomb corrected local spin density approximation (LSDA+U) method for better accounting of the correlation between the 4*f* electrons. The optimized lattice constants and internal cell parameters are in agreement with the available data. Self consistence band structure calculations show that Ni-3*d* states remains in valance band and dominant below the E_F, while Dy-5*d* and 4*f* states mainly contributes above Fermi Energy (E_F) in $DyNi_{5-x}Si_x$ ($x=0, 1, 2$) compounds. We also find that when silicon for nickel substitution takes place ($DyNi_4Si$), there is a gradual hybridization of Ni-3*d* and Si-3*p* states results, nickel moments decrease rapidly in agreement with the experiment. Optical spectra shows the main absorption peak around 4 eV depends on the substituent concentration and could be due to transition from hybridized band (Ni-3*d* and Si-3*p*), below E_F to free Dy-4*d* states. Frequency-dependent refractive index, $n(\omega)$, and the extinction coefficient, $k(\omega)$, of $DyNi_{5-x}Si_x$ ($x=0, 1, 2$) are also calculated for the radiation up to 14 eV.

1. Introduction

Rare earth (R) intermetallic compounds of the $CaCu_5$-type RNi_5 are prominent in the large variety of their magnetic structures and electronic characteristics. The potential characteristics of these compounds motivate their engineering prospective as functional materials for permanent magnets and magnetothermal applications, as well as for devices based on magnetostriction and magnetoresistive effects [1–3]. The explicit features in the magnetic and electronic properties of the RNi_5 intermetallic compounds are associated with the Ni-3*d* bands being practically fully occupied by 5*d* electrons of the outer shells of R atoms, which make the contribution of nickel atoms to the spontaneous magnetic moment weak. Significant change in the physical properties of the RNi_5 compounds take place when nickel is substituted for by atoms of other *d* or *p* metals as a results of the strong effect an impurity exerts on the parameters of the electronic structure, crystal field, and exchange interaction. It has been established in the past that an increase in the number of electrons in the conduction band in $CaCu_5$-type pseudobinary $RNi_{5-x}M_x$ alloys ($x \leq 3$) with M=(M=Al, Cu, Fe, Co) alloys, leads to significant changes in the physical properties and exhibit nonmonotonic concentration dependences of the crystalline, electronic, magnetic, and thermodynamic characteristics [4–6].

Numerous experimental [7–10] and theoretical [11–13] studies of electronic and magnetic properties have been reported on these $CaCu_5$ – type pseudobinary rare earth alloys in the past. Bajorek et al. [7,8] measured the magnetic susceptibility, electrical resistivity, crystal and electronic structure for $GdNi_{5-x}Cu_x$ system and observed that when nickel is substituted for copper atoms the cell volume increases and Curie temperature is weakly dependence on concentration *x*. Optical properties of intermetallic isostructural compounds $LaNi_{5-x}Cu_x$ ($x=0$, 0.6, 1, 1.2) have been studied in the spectral range from 0.22 to 15 m using the ellipsometry method by Knyazev et al. [9] and found that the substitution of copper for nickel leads to local changes in the optical conductivity spectra. Lukoyanov and Knyaz [11] performed Magnetic measurements and XPS studies on $RNi_{5-x}Al_x$ and $RNi_{5-x}Cu_x$ (R=La, Nd, Tb, Dy) compounds. They observed that the nickel moments, in low temperature range, decrease when increasing aluminum or copper content and are practically nil for $x>1$. Miletic et al. [14] prepared $DyNi_{5-x}Ga_x$ alloys and studied by X-ray powder diffraction. A single phase region has been observed and it exists up to the composition $DyNi_2Ga_3$ in the $DyNi_{5-x}Ga_x$ system. They also observed a decrease in the hydrogen capacity and the equilibrium pressure with increasing gallium content. Burzo et al. [15] studied on the magnetic properties and electronic structures of $DyNi_{5-x}Al_x$ compounds. Analysis of the experimental data was

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Table 1
Atomic positions for the 2*a*, 4*i*, 2*c* and 4*f* sites of the YNi_4Si-type $DyNi_{5-x}Si_x$ (x=0,1,2) compounds.

$DyNi_5$	Site	x/a	y/b	z/c	$DyNi_4Si$	Site	x/a	y/b	z/c	$DyNi_3Si_2$	Site	x/a	y/b	z/c
Dy	2*a*	0	0	0	Dy	2*a*	0	0	0	Dy	2*a*	0	0	0
Ni1	4*i*	0	[a]y_{Ni1}	0	**Ni1**	4*i*	0	[a]y_{Ni1}	0	**Si**	4*i*	0	y_{Si}	0
Ni2	2*c*	0	1/2	1/2	Si	2*c*	0	1/2	1/2	Ni2	2*c*	0	1/2	1/2
Ni3	4*f*	1/4	1/4	1/2	Ni3	4*f*	1/4	1/4	1/2	Ni3	4*f*	1/4	1/4	1/2

[a] y_{Ni1}=0.3343 ($DyNi_5$), y_{Ni1}=0.3411 ($DyNi_4Si$), y_{Si}=0.3404 ($DyNi_3Si_2$).

done in correlation with computed band structures and found that when replacing nickel with aluminum there is a gradual hybridization of Ni 3*d* and Al 3*p* bands, and as a result the nickel moments at 0 K decrease and are nil for x > 2. The refractive (n) and absorption (k) indices of intermetallic $DyNi_{5-x}Al_x$ compounds (x=0, 0.5, 1, 1.5, 2) have been measured by Knyazev et al. [16] using ellipsometry at room temperature in the spectral range of 0.22–15 μm. They observed that the three-peak structure of the optical conductivity spectra for $DyNi_5$ is gradually modified with an increase in x and has a single wide peak for the $DyNi_3Al_2$ ternary compound.

Recently Morozkin et al. [17,18] have made modification of the $CaCu_5$-type rare earth compound via solid solution and established the new YNi_4Si-type structure of RNi_4Si (R=Y, La, Ce, Sm, Gd-Ho) compounds. The YNi_4Si structure is a new structure type, which is an orthorhombic derivative of $CaCu_5$ structure. They observed the order ferromagnetic nature of $GdNi_4Si$ and $DyNi_4Si$ compounds at 25 and 19 K, respectively and calculated the magnetocaloric effect of YNi_4Si-type RNi_4Si in terms of isothermal magnetic entropy change. In our earlier study [19], we reported the structural, electronic and optical properties of new YNi_4Si-type RNi_4Si (R=La and Gd) compounds using self-consistent full-potential augmented plane wave (FP-LAPW) [20,21] method. Analysis of the calculated band structure of $LaNi_4Si$ and $GdNi_4Si$ compounds suggest that Ni-3*d* states mainly contribute to density of states (DOS) from −5.0 eV to the Fermi level which is consistent with experiment and previously reported result by Kowalczyk et al. [22] having hexagonal $CaCu_5$ structure.

In order to study the structural, electronic and optical properties of YNi_4Si-type $DyNi_{5-x}Si_x$ (x=0, 1, 2) compounds first principle calculations are performed. To author's knowledge theoretical and experimental study on electronic and optical properties of YNi_4Si-type $DyNi_{5-x}Si_x$ compounds have not been addressed. The present study would also explore the role of substitutional change of silicon in place of nickel on structural, electronic and optical properties as well as encourage the measurement of these properties on YNi_4Si-type $DyNi_{5-x}Si_x$ (x=0, 1, 2) compounds.

2. Computational details

Self-consistent FP-LAPW [20,21] calculations on $DyNi_{5-x}Si_x$ were carried out using WIEN2k code [23]. We considered a number of basic functions up to $R_{MT} \times K_{max}$=7, where RMT is the minimum radius of the muffin-tin spheres and K_{max} gives the magnitude of the largest K vector in the plane wave basis, to achieve an adequate exchange between accuracy and cost. In order to keep the same degree of convergence, we kept the values of the sphere radii and K_{max} constant over all the crystal geometries considered. The muffin-tin radii RMT for Dy, Ni and S to be 2.5, 2.32 and 1.84 bohr, respectively, have been selected and the APW + lo basis set [24], with additional 5*s* and 5*p* local orbitals for the rare earth atom is used. Additionally, the valence wave functions inside muffin-tin spheres are expanded up to l_{max}=10. The LSDA functional is used for exchange and correlation effects. For better accounting of the correlation between the 4*f* electrons, Anisimov et al. [25] introduced the self consistent LSDA+U method. This method explicitly includes the on-site Coulomb interaction term in the conventional Hamiltonian. Harmon et al. [26] determined the numerical values of the parameters of the direct Coulomb (U=6.7 eV) and exchange (J=0.7 eV) interaction for Gd. These numerical values of the parameters have been used to perform the calculations. The dependence of the energy on the number of k points in their reducible wedge of the Brillouin zone (IBZ) has been checked, and the size of the mesh has been set to 12 × 12 × 12 Monkhorst and Pack [27] k-point mesh, which yields 301 k-points in the IBZ. We considered the self-consistency to be reached when the total energy difference between successive iterations is $< 10^5$ Ry per formula unit. The convergence was also checked with a refined mesh in the IBZ with no appreciable change in energy or properties. The modified tetrahedron method [28] has been used to perform the **k** space integration. We used a broadening of 0.1 eV to simulate the experimental finite lifetime effects.

The Crystal arrangement of $DyNi_{5-x}Si_x$ (x=0, 1, 2) compounds is YNi_4Si-type structure with space group *Cmmm*. In $DyNi_5$ compound nickel atoms are located at three non equivalent positions. Rare earths occupy the 2*a* site (0, 0, 0) and Ni^1 is located in the 4*i* site (0, y_{Ni1}, 0), where internal cell parameter (y_{Ni1})=0.3415 [17]. Ni^2 and Ni^3 atoms are statistically distributed over 2*c* site (0, 1/2, 1/2) and 4*f* site (1/4, 1/4, 1/2), respectively. Site occupation by Dy and Ni atoms in $DyNi_{5-x}Si_x$ (x=1, 2) is similar to the $DyNi_5$, except 2*c* and 4*i* site which is doped with silicon atoms in $DyNi_4Si$ and $DyNi_3Si_2$, respectively. The Wyckoff positions and unit cell data are presented in Tables 1 and 2, respectively. We have performed calculations for the ferromagnetic phase, as $DyNi_{5-x}Si_x$ compounds are ferromagnetic at low temperatures. The electronic structure of $DyNi_{5-x}Si_x$ compounds is studied within the ab initio approach.

Table 2
Equilibrium lattice parameters (*a*, *b*, *c*, *b*/*a* and *c*/*a*) (in a.u.), internal cell parameters (y_{Ni1}/y_{Si}), cell volume V (in a.u.^{3}), bulk modulus B_0 (in GPa), and its pressure derivative B_0' for $DyNi_{5-x}Si_x$ (x=0, 1, 2) at 0 GPa and 0 K (This work) and at 0.1 GPa and 298 K [17].

		a	*b*	*c*	*b*/*a*	*c*/*a*	y_{Ni1}/y_{Si}	Vol	B_0	B_0'
$DyNi_5$	This work	9.24380	16.01076	7.52172	0.812586	1.734751	0.3343	556.60900	142.3509	2.8986
	Expt. [17]	9.21354	15.95835	7.49710	0.813704	1.732053	0.3333	551.16164		
$DyNi_4Si$	This work	9.42427	15.31007	7.37433	0.808758	1.564982	0.3411	531.82690	180.2626	5.3110
	Expt. [17]	9.53914	15.49669	7.46422	0.782483	1.624536	0.3415	551.70089		
$DyNi_3Si_2$	This work	9.42126	15.30520	7.37199	0.679411	1.818965	0.3404	531.45988	175.5218	4.8594